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(54) Name of Invention: Very Pure Tantalum Material, its Method of Manufacture and its Use in Tantalum Targets

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Specifications

1. **Name of Invention:** Very Pure Tantalum Material, its Method of Manufacture and its Use in Tantalum Targets

2. Scope of Patent Application

(1) A high-purity tantalum material characterized by its oxygen content being 50ppm or less, and its content of the elements iron, nickel and chrome being 0.05ppm or less.

(2) A method of manufacturing the high-purity tantalum material described in Application Item 1, characterized by tantalum refined by iodide decomposition, being fused in a vacuum of 5×10^{-5} mbar or less.

(3) A method of manufacturing the high-purity tantalum material described in Application Item 2, characterized by fusing it by the electron-beam fusion method.

(4) A tantalum target characterized by using the high-purity tantalum material described in Application Item 1.

3. Detailed Explanation of Invention

Purpose of Invention

Field for Commercial Utilization: This invention relates to high-purity tantalum used in semiconductor devices and to its method of manufacture and use as a sputtering target.

Usual Technology: Currently, thin tantalum oxide (Ta_2O_5) film is being studied as a VLSI storage capacitor material in lieu of SiO_2. Ta_2O_5 has a specific [illegble] about six times that of SiO_2, thus enabling one to make the capacitor area smaller. However, tantalum oxide gives more current leaks than silicon dioxide, and its effective specific [illegible] declines when it is made into thin film. For such reasons it has not been used heretofore. This thin tantalum oxide film is formed by such methods as reactive sputtering or CVD. In reactive sputtering it is formed by sputtering in a mixed argon/oxygen atmosphere with a tantalum target.

For the VLSI's electrode material, a high fusion-point metallic silicide such as tungsten is being used; but tantalum silicide is being considered as the next electrode material. There are several ways to form tantalum silicide film. A pure tantalum target is used to form tantalum silicide by applying tantalum film to polysilicon and then causing the tantalum to react with the Si.

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* [Due to the poor original copy, subscript and superscript numbers and symbols often ar illegible and are guessed at. Also some terms are illegible. Translator]

Impurities such as the following in metallic material generally used in VLSIs adversely affect them, so that a high purity is required:

a. Alkaline metals such as Na & K (weaken interface traits)
b. Radioactive elements such as U & Th (soft errors)
c. Heavy metals such as Fe & Cr (interface junction trouble)

However, the tantalum now made commercially is tantalum ingot made by melting tantalum refined by such means as electrolysis and then processing it into targets. But, it is unusable for LSIs, as it contains the above-described elements in quantity. Even in minute quantities, these elements have an adverse effect on the traits of [semiconductor] elements. So, it has become even more necessary to manufacture tantalum targets in which the tantalum is further purified.

Problem the Invention Seeks to Resolve: Tantalum produced by the usual techniques has a high impurity content and cannot be used as LSI material. So, this invention has the purpose of providing high-purity tantalum material useable in semiconductor devices and a method to manufacture it and the tantalum targets which use it.

Makeup of the Invention

Means to Resolve Problems: That is, this invention is a high-purity tantalum material and tantalum targets using it which are characterized by an oxygen content of 50ppm or less and iron, nickel and chrome elements at 0.05ppm or less content.

This invention also is a method of manufacturing this high-purity tantalum, a method characterized by using the iodide decomposition method to break down commercial tantalum in a vacuum of 5×10^{-6} mbar.

Effects

With the degree of integration in LSIs increasing and elements being miniaturized, signal [illegible] from increased electrical resistance is becoming a problem. In such a context, the next electrode material being sought will have low electrical resistance. And yet, oxygen in high fusion-point metallic silicide films raises electrical resistance. Particularly in recent years, contamination in the film-production process has become very slight, with impurities in the targets reflecting impurity concentrations

in the film. So, we carefully investigated oxygen concentrations in the tantalum and the specific resistance of the reactive tantalum silicide.

We first formed an 0.1μm tantalum film on polysilicon and lamp-annealed at 1000°C to form a tantalum silicide film. The oxygen concentrations in the tantalum targets were respectively 30ppm, 50ppm, 100ppm, 250ppm and 400ppm. Other impurities were in nearly equal concentrations. This showed a connection between the specific resistance of the tantalum silicide film we had formed and the oxygen concentration, as in Table 1. As is clear from this result, when oxygen is present at 100ppm or more, specific resistance rises as the oxygen concentration rises. This means that to keep the reactive tantalum silicide film's specific resistance low, the oxygen concentration in tantalum targets must be 50ppm or less.

Table 1

	Fe	Ni	Cr	Al	Mn	Mg
Target A	<0.05	<0.05	0.05	<0.01	<0.01	0.01
Target B	0.2	0.1	0.2	<0.1	<0.01	0.01
Target C	10	5	15	<0.1	<0.01	0.01

When tantalum oxide is used as storage capacitor material in lieu of silicon dioxide, the biggest problem is that leaking currents are greater. Quite recently it was found that leaking currents are related to impurity concentrations in the targets. Particularly if such concentrations are extreme, the effects of minute impurity amounts become conspicuous. So, to investigate the effects of heavy-metal impurities on leaking currents, we made thin tantalum oxide films by reactive sputtering, using three kinds of targets by different fabrication processes. Their respective nickel and chrome concentrations are shown in Table 1.

The concentrations of elements other than those shown in this Table 1 were nearly identical in A, B and C. Also, the film thickness of all was about 15nm. The relationship between their respective film fields and the density of leaking currents is shown in Table 2. Compared to what was used in targets B and C, tantalum oxide made into film used in target A, which had the lowest concentration of iron, nickel and chrome, has very low leaking currents; and the reduction of heavy metallic elements effectively restrains leaking currents. So, their concentration needs to be 0.05ppm or less.

Thus, tantalum targets for VLSIs need reductions in sodium, phosphorus, uranium and thorium; but reductions must also be made in concentrations of oxygen and heavy metal elements. High-purity targets meeting such specifications can be produced by the following processes.

The above-described high purity tantalum targets can be obtained from high-purity tantalum material produced by combining the iodide decomposition method and electron beam melting. This iodide decomposition method is a kind of chemical transport and is used to refine tantalum as well as titanium, zirconium, hafnium and other active metals. The refining is done using the following reactions (1) and (2).

$$Ta + 5/2\ I2 \rightarrow TaI5\ (300\sim700°C) \qquad (1)$$

$$TaI5 \rightarrow Ta + 5/2\ I2\ (800\sim1500°C) \qquad (2)$$

That is, with the iodine, tantalum at 300~700°C forms TaI_5 (Equation 1). And, TaI_5 has the nature of breaking down into elemental tantalum at temperatures of 800~1500°C, as shown in equation (2). Figure 3 is a diagram of one example of the device for producing high-purity tantalum with this iodide decomposition method. In the figure, 1 is a reaction vessel containing raw tantalum 4 and elemental iodine 5. 2 is a filament connected to power source 6 by connectors 7a and 7b. Heating to 800~1500°C is done electrically. The entire reaction vessel is put into heat-resistant vat 3 and kept at 300~700°C. In this temperature range the above-described equation (1) reaction causes the tantalum and iodine to react and produce TaI_5. TaI_5 on the filament will break down into iodine and tantalum as in equation (2) and be deposited. The iodine again reacts with the tantalum, which is transported to the filament. Now impurities in the raw tantalum will remain in the raw material, being less reactive with iodine than the tantalum, so that in principle only pure tantalum is transported to the filament. Very pure tantalum from the iodide decomposition method is refined by this principle. The [illegible] pressure of metallic iodides depends greatly on temperature; and at temperatures (300~700°C) producing the tantalum iodide the [illegible] pressure of the iodides of K, U, Th, Fe and Cr is very low so that the refining effect becomes high.

On the other hand, electron-beam decomposition is a way to break down impurities by using differences in [illegible] pressure. Sodium and phosphorus, with a high [illegible] pressure, have an especially high refining effect. Titanium refined by the above-described iodide decomposition can be further refined by electron-beam decomposition. Because it

is done in a high vacuum of 5×10^{-6} mbar, fusing can make high-purity tantalum ingots with little contamination by oxygen or nitrogen. By manufacturing and mechanical processing of such ingots, one can complete tantalum targets of any shape.

Application Example

We placed commercial tantalum and iodine into the Hasteroi [per Japanese phonetics -- Translator] reaction vessel shown in Figure 3 and heated them in a [illegible] vat to about 550°C. Heating a tantalum filament 2.0mm in diameter to 1000°C by directly passing an electrical current through it, we caused the tantalum to deposit [?? Assumed from context. --Translator] on the filament. After about 105 hours, the filament had grown to a diameter of 25mm. High-purity tantalum thus produced was further refined by doing electron-beam decomposition in a vacuum of 1×10^{-6} mbar. Then we processed it mechanically to finish it into tantalum targets. Table 2 shows the amounts deposited after electron-beam fusing following the raw material/iodide decomposition.

Table 2

(ppm)

	Fe	Ni	Cr	Nb	N	O	Na	K	U	Th
Raw material	40	20	36	120	200	770	3	3	0.05	0.05
After iodide decomposit'n	1	2	1	30	20	40	<.1	<.1	<.001	<.001
After iodide decomp. + electron beam fusing	<.05	<.05	.05	<10	10	30	<.1	<.1	<.001	<.001

As shown by this table, one can greatly reduce the content of the respective elements with a combination of iodide decomposition and electron-beam fusing.

We then used these targets and sputtering to form an 0.1mm Ta film on polysilicon and lamp-annealed it at 1000°C to form the tantalum-silicide film. We used the four-terminal method to measure the film's specific resistance and found 35.2 $\mu\Omega$·cm.

Again, using the above-described targets, we did reactive sputtering to form Ta_2O_6 film. We applied an electrical field to measure the leaking current at that time and got a leaking current density of 1×10^{-3} A·cm^{-7} at 2.5μV.

Effectiveness of Invention

With this invention, tantalum made by iodide decomposition is subjected to electron-beam fusion to enable the manufacture of tantalum material of higher purity than by the usual process and yield tantalum targets of high purity.

4. Simple Explanation of Figures

Figure 1 is a graph showing the relationship between the specific resistance of reactive tantalum silicide film and oxygen concentrations in tantalum targets.

Figure 2 is a graph showing the interdependence of tantalum oxide film's leaking currents and field strength.

1 ..... Reaction vessel
2 ..... Filament
3 ..... [illegible] vat
4 ..... Tantalum
5 ..... Iodine
6 ..... Power source
7a, 7b .. Connectors

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